

Measuring sulphur in the electrolyte of aluminium reduction cells

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Abstract



Impurities are known to affect aluminium production. To study the effect of impurities in this industry, it is important to accurately quantify their concentration. This work focuses on sulphur quantification in cryolite-alumina melts. X-Ray Fluorescence (XRF) was selected as a method and its performance was evaluated by adding predetermined amounts of sulphur to the melt in the form of sodium sulphate (Na_2SO_4). The amount of added total sulphur ranged from 100 to 1200 ppm. Based on linear regression analysis, XRF exhibited a coefficient of determination of 0.99. Systematic overestimate by a factor of 1.1 for sulphur was observed. XRF performance was compared with Ion Chromatography (IC) and Inductive Coupled Plasma Optical Emission Spectrometry (ICP-OES). Comparison with IC and ICP-OES revealed discrepancies of up to 70 % in concentration, which may be due to sample preparation techniques. To obtain representative samples with least contamination of carbon dust, a modified sampling device with a closing mechanism was adapted from Rolseth [1] and tested. The device delivered reproducible samples with a sulphur concentration of 94.8 ± 11.0 ppm. The iron spatula used as a standard sampling tool at the aluminium plant produced 461 ± 370.2 ppm from the same cell. Samples were analysed for phosphorous in the XRF along with the sulphur. Phosphorus is one of the known detrimental impurities in aluminium production. The phosphorus concentration was not influenced by the sampling technique.

Keywords: Sulphur; sodium sulphate; phosphorus; analytical methods.

1. Introduction

Some impurities have negative effects on aluminium production both on the production process and the final products. Depending on their nature, impurities can cause excess carbon consumption or deterioration of materials, change electrolyte composition, reduce current efficiency, and affect metal quality [2]. One of the most studied impurities, known for its detrimental effect on current efficiency, is phosphorus. Current efficiency can be reduced by as much as 1 % for each 100 ppm of phosphorus present in the electrolyte [3 - 9]. Within the last decade, another impurity – sulphur – has been receiving increased attention. This was spurred by a change in crude oil quality, which resulted in higher sulphur concentrations in anodes [10]. Moderate levels of sulphur in the anodes have been considered beneficial as sulphur protects the anodes from air burn and CO_2 reactivity [11 - 14]. However, recent work studying the effect of sulphur on current efficiency shows that sulphur also may reduce current efficiency by 1.8 % for every wt% of sulphur in the anode (sulphur concentrations ranged from 0 to 3.82 wt% of sulphur for these experiments) [15]. As sulphur in anodes was shown to have an effect in a laboratory cell, it is also of interest to study the effect of sulphur in the electrolyte on the electrolysis. For this end, reliable measurements of sulphur concentration are required.

Literature treating the analysis of sulphur in cryolite-alumina samples is scarce [16 - 19]. Available literature uses either wet chemistry or ion chromatography. These methods are time

consuming and more suitable for measuring high levels of sulphur. Sample preparation is complex and can introduce significant uncertainties into the measurements. The objective of our study was to test a different method for sulphur analysis in cryolite-alumina melts, X-Ray Fluorescence (XRF) which is available at many aluminium plants. Sulphur, because of its atomic number and associated radiation energies, is particularly well suited for XRF [20]. XRF provides fast multi-elemental analysis, without involvement of chemical attack accurate values are consistently obtained for total sulphur regardless of the sulphur mineral species [20 - 22]. Samples are not destroyed during the analysis and can thus be used for comparison with other methods. XRF has been widely used in a number of other fields. Of particular interest are measurements of sulphur in petroleum products, which contain sulphur within their structure [23, 24].

To achieve our goal, we added known amounts of sodium sulphate into solidified electrolyte samples taken from aluminium cells and analysed the samples by XRF. We compared the results to measurements obtained by different analytical techniques, in particular Inductive Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Ion Chromatography (IC). A recently published paper [19] has verified the accuracy of IC for measurements from cryolite melts and reported satisfying results for concentrations below 1000 ppm with 1.1 % uncertainty. ICP-OES has been recognized by having far superior detection limits and for providing accurate, rapid results for sulphur [25, 26]. To exclude the possibility of sample incompatibility, identical samples were utilized for three methods.

In order to collect representative samples from the cryolite-alumina melts, a sampling device design equipped with a sampling mechanism was adopted from Rolseth [1], modified and tested. This sampling device can take samples from a predetermined location, for example from the bulk of the electrolyte where least carbon dust is present, and the closing mechanism prevents mixing during extraction. Since XRF can also measure phosphorus concentration during the sulphur analysis, the effect of the sampling device on phosphorus content is also reported.

2. Experimental procedure

Automated equipment from Herzog Maschinenfabrik was used for sample preparation. The device is equipped with a sample magazine (Mach.No: MA12683-1-1), a metal detector (HP-CA/M/TD (Mach.-No.: 12683-3-1), a miller (HP-MA (Mach.-No.: MA12683-6-1), and a tablet press (HP-PA (Mach.-No.: MA12683-10-1). A cellulose preparation pallet weighing 0.20 g for each 25 g of sample was added to improve grinding and binding during tablet pressing.

Verification of XRF accuracy: After the samples were milled and well mixed, 5 representative samples were taken for measurement of background sulphur concentration. The remaining samples were spiked with known quantities of sulphur. The following samples were created: 5 samples spiked with 100 ppm of sulphur, 10 samples with 200 ppm of sulphur, 8 samples with 300 ppm of sulphur, and 5 samples with 1 000 ppm of sulphur. The last 3 samples contained 1 180 ppm of sulphur in the crushed bath. All the 31 samples were analyzed by XRF. The 5 reference samples without additional sodium sulphate were also analyzed by XRF, and the amount of sulphur from these samples was subtracted from the sulphur concentration in the spiked samples.

Comparison of XRF with other methods: The solidified electrolyte was crushed into powder and well mixed. Five reference samples (without additional sodium sulphate) were taken. Subsequently, 0.44 wt% of sodium sulphate (1000 ppm of sulphur) was added into the powder

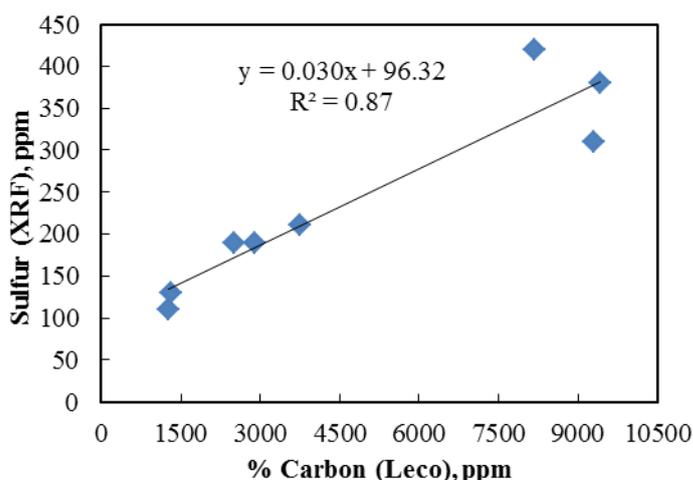


Figure 5. Sulphur concentration in the electrolyte determined by XRF as a function of the carbon content in the electrolyte determined by LECO.

4. Conclusions

Determining the sulphur concentration in cryolite melts was found to be very challenging. Carbon dust has the largest influence on the concentration of sulphur in the electrolyte. XRF showed a coefficient of determination $R^2 = 0.99$ and an overestimate by a factor of 1.1 was observed. However, when compared with IC or ICP-OES methods discrepancies of up to 70 % between sulphur analyses were observed. More work has to be done to check the reliability of IC and ICP-OES implemented here. A modified Rolseth sampling device can help to eliminate carbon dust and obtain representative samples with good reproducible results. The sulphur concentration was 94.8 ± 11.0 ppm using the modified Rolseth device. However, the standard iron spatula used at aluminium plants produced 461.4 ± 370.2 ppm from the same cell.

The phosphorus concentration in the electrolyte did not show any dependency on the sampling technique and the presence of carbon dust.

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